

Nanostructured $\text{Li}_4\text{Ti}_5\text{O}_{12}$ Powders and Method of Making the SameCROSS REFERENCE TO RELATED APPLICATIONS

5 This application claims priority of US provisional application No. 60/265,290
filed February 1, 2001.

BACKGROUND OF THE INVENTION

10 This invention relates to the production of nanostructured or ultrafine particles
(i.e. particles of less than 1 micron and preferably in the size range of 25 – 500 nm) of
lithium titanate ($\text{Li}_4\text{Ti}_5\text{O}_{12}$) a compound, which is an important anode material for
rechargeable energy storage devices such as Li based batteries and asymmetric hybrid
cells. The electrochemical performance of nanostructured lithium titanate exceeds that of
15 coarse (large) size particles of the same material.

20 Nanomaterials-derived products are being actively pursued for use in a wide
range of applications, including electrochemical energy storage and generation, chemical
sensors, optoelectronics, semiconductors, wear and scratch resistant coatings, and heat
transfer. The interest stems from the fact that researchers see immense potential for
improving functional properties of components and devices by nanostructuring. In some
cases, the use of nanoparticles as feedstock material can facilitate processing of an
improved end product at a lower cost. However, while the use of nanoparticles as

starting material can lead to benefits in a number of applications, researchers must tailor the structure and composition of the starting powder in order to maximize the property enhancements and performance and realize the true potential of nanomaterials.

5 Over the past several years, a number of techniques have been developed for the production of ceramic nanoparticles. These include: laser ablation, microwave plasma synthesis, precipitation from a solution, spray pyrolysis, plasma arc synthesis, hydrodynamic cavitation, and gas condensation using either a physical evaporative source or chemical precursors. Vapor phase processes are capable of producing well-
10 defined spherical nanoparticles with narrow particle size distribution. Several single component oxides can be produced by an atmospheric flame process at low cost. However, it is extremely difficult to control the composition of multi-component ceramic powders because of the significant variations in the vapor pressures of different constituents. On the other hand, solution-based processes have an excellent control on the
15 composition, but particle characteristics are not as good as those of produced by any of the vapor phase process. The synthesis method discussed in this patent application bridges the gap between liquid and vapor phase processing routes to produce nanostructured doped/multi-component ceramic powders with well-defined particle characteristics.

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SUMMARY OF THE INVENTION

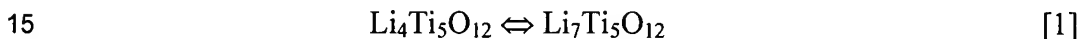
This invention relates to nanostructured (or ultrafine) $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders with a spinel-type structure with improved Li-ion diffusion. $\text{Li}_4\text{Ti}_5\text{O}_{12}$ can also be written as

$\text{Li}(\text{Li}_{0.33}\text{Ti}_{1.66})\text{O}_4$. A spinel structure consists of eight subcells, and each subcell has four oxygen atoms, four octahedral interstices and eight tetrahedral interstices. In each elementary cell, two octahedral sites are filled with Li and Ti atoms in a ratio of 0.33: 1.66 and one tetrahedral site with one Li atom.

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These materials are of particular interest as anode for Li – based rechargeable energy storage devices. The present invention includes nanostructured (or ultrafine) $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders and method of making the same. The present invention relates to a general method for the production of nanostructured (or ultrafine) $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders.

10 $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is an attractive negative electrode material for secondary rechargeable energy storage devices wherein Li-ions are cycled in and out during a charging and a discharging process of the device. Three Li ions can be inserted into the structure according to the reaction:



The reaction occurs at approximately 1.5V vs metallic lithium, thereby providing a relatively safe electrode system compared to carbon in which insertion of Li ions occurs at a voltage range of 0.0 to 0.5 with respect to Li. However, safety is gained at the expense of cell voltage and energy density. From a structural viewpoint, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is an ideal anode for Li-based rechargeable batteries, because the Li insertion into the cubic $\text{Li}_4\text{Ti}_5\text{O}_{12}$ spinel structure occurs without any change in the lattice parameter (8.36 Å); thereby providing an extremely stable electrode structure. Negative electrodes made of

Li₄Ti₅O₁₂ material can undergo many hundreds of cycles without structural disintegration. Moreover, lithium insertion causes a first-order displacement of the tetrahedrally-coordinated Li ions in the Li₄Ti₅O₁₂ spinel structure into octahedral sites to generate the ordered rock-salt phase Li₇Ti₅O₁₂. The insertion (and extraction) of lithium is thus a two-phase reaction which provides a constant voltage response at ~ 1.5 V. Furthermore, the voltage of a Li/ Li_{4+x}Ti₅O₁₂ cell changes abruptly at the end of discharge and charge. Thus, a Li_{4+x}Ti₅O₁₂ spinel electrode provides very sharp end-of-charge and end-of-discharge indicators which is useful for controlling cell operation and preventing overcharge and overdischarge.

Several of the commercial applications, including hybrid electric vehicles, uninterruptable power sources (UPS) and power tools, require that batteries be able to charge to their full capacity in a short period of time, less than 30 minutes. However, anodes made of micron-sized or larger Li₄Ti₅O₁₂ spinel particles do not exhibit good rate capability because of poor Li-ion diffusion.

In the past, attempts have been made to improve the electronic conductivity of Li₄Ti₅O₁₂ phase by substituting Li-ions on octahedral sites with Mg or Al. US Patent No. 6,221,531 to Vaughey et al. discloses electrically conductive Li[Ti_{1.67}Li_{0.33-y}M_y]O₄ (M = Al or Mg) powders. However, improving electronic conductivity of Li₄Ti₅O₁₂ phase will not enhance its charging rate capabilities as the electronic conductivity of Li₄Ti₅O₁₂ anode is important only during the discharging process. The present invention focuses on

developing $\text{Li}_4\text{Ti}_5\text{O}_{12}$ materials with high Li-ion diffusion capabilities, which implies high ionic conductivity, and hence high charge rate capabilities.

BRIEF DESCRIPTION OF THE DRAWINGS

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For a better understanding of the invention, reference is made to the following drawings which are to be taken in conjunction with the detailed description to follow in which:

Figure 1 is a photomicrograph of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles produced in accordance with the present invention.

Figure 2 is the x-ray diffraction pattern of the particles produced in accordance with the present invention.

Figure 3 is a schematic diagram of the present process to produce nanostructured $\text{Li}_4\text{Ti}_5\text{O}_{12}$.

Figure 4 is a photomicrograph of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles before heat treatment.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

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In one aspect, the invention provides ultrafine powders of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ with particles in the size range of 25 – 500 nm. The average size of particles is about 500 nm or less, preferably about 300 nm or less. In another aspect, particles are composed of nanocrystallites, which have an average size about 30 nm. This invention also includes the method of producing these ultrafine $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles. The process utilizes (i)

nanoparticles of TiO_2 , (ii) a lithium salt such as, lithium nitrate, lithium iodide, lithium hydroxide, lithium chloride and lithium carbonate, and (iii) an organic solvent with a boiling point in the range of 70 – 230 °C. The process carried out at pressures in the range of 0.5 to 10 atmospheres. An inorganic salt of Li is mixed with TiO_2 nanoparticles (20 - 25 nm) in an organic solvent such as, hexanol. The solution is heated (preferably in a refluxing operation) to a high enough temperature (70 – 230 °C) at a pressure to facilitate the diffusion of Li ions in to nanoparticles. After completion of the reaction, the powder is heat treated (annealed) in O_2 at a relatively low temperature (500 – 800 °C) to form the desired phase. The heat treatment can also take place in an atmosphere containing an inert gas such as, N_2 , He or Ar. Powders were annealed at several temperatures to ensure the complete transformation to a $\text{Li}_4\text{Ti}_5\text{O}_{12}$ phase. Once the transformation to $\text{Li}_4\text{Ti}_5\text{O}_{12}$ phase has completed, further high-temperature annealing by promoting the sintering between particles will form coarse particles. Therefore, the lowest possible annealing temperature needs to be utilized in order to maintain the ultrafine nature of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles.

In contrast to solid state synthesis techniques, the present process leads to ultrafine particles, which are composed of nanocrystallites. Additionally, this process enabled us to produce discrete particles with precise composition, which was not possible by either conventional sol-gel or vapor phase processes. The process described in the present invention utilizes an organic solvent with a boiling point of 79 °C or more, preferably about 125 °C or more and more preferably from about 150 to 230 °C. The process for making ultrafine multi-component oxide particles described in the present

invention is quite different from the well-known hydrothermal process in which particles are produced by heating chemical precursors or precursor particles, which are dissolved or suspended in water, at a high pressure (> 4 atmospheres) for an extend period of time.

5 Electrodes made of nanostructured (or ultrafine) $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders in both $\text{Li}/\text{Li}_4\text{Ti}_5\text{O}_{12}$ test cells and asymmetric hybrid cells have shown excellent rate capabilities as shown by: Amatucci, Glenn G., Fadwa, Badway, Pasquier, Aurelien D., and Zheng, T., “An Asymmetric Hybrid Nonaqueous Energy Storage Cell”, *Journal of the Electrochemical Society*, 148, A930 (2001). Asymmetric hybrid cells made with ultrafine
10 $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders as anodes charged to 92% of their initial capacity at a rate of 10C Cells made with ultrafine $\text{Li}_4\text{Ti}_5\text{O}_{12}$ as electrodes discharged to 90% of their initial capacity at a rate of 10C (wherein 1C = 1 hr charge or discharge, 10C = 6 min. charge or discharge), while $\text{Li}/\text{Li}_4\text{Ti}_5\text{O}_{12}$ cells with electrodes consisting of coarse $\text{Li}_4\text{Ti}_5\text{O}_{12}$ discharged only to 30% at a rate of 10C. Furthermore, electrodes made of $\text{Li}_4\text{Ti}_5\text{O}_{12}$
15 powders, which are prepared by the solid-state reaction between Li_2CO_3 and nano- TiO_2 , discharged only to 75% of their initial capacity at a rate of 10C. Smaller particles have shorter diffusion distances for intercalated Li-ions, resulting in a higher charge rate for intercalated anodes.

20 Ultrafine $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles having diameters substantially less than a micron have been produced. The preferable particle size is in the range of 50 – 400 nm as shown in the TEM photomicrograph of Fig. 1. Ultrafine $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles are also composed of nanocrystallites: the preferable nanocrystallite size is in the range of 20 – 100 nm. The

average crystallite size of 30 nm was determined from the broadening of two X-ray peaks: $2\theta = 18.5^\circ$ and 56.5° in the x-ray diffraction pattern of Fig. 2.

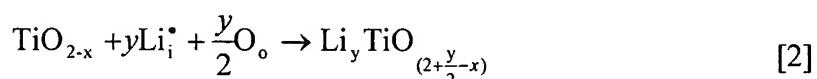
Ultrafine particles of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ are formed by a wet chemistry method in which an inorganic lithium salt is mixed with TiO_2 nanopowders, which have an average primary particle size 100 nm or less, preferably 50 nm or less, and most preferably 25 nm or less. ($\text{Li}_4\text{Ti}_5\text{O}_{12}$ particle formation does not depend on how the TiO_2 nanopowders have been produced). The mixture of lithium salt and TiO_2 nanopowders is refluxed in a high boiling point organic solvent in order to facilitate the diffusion of Li ions into nanoparticles. Since the precursor particles have very high surface/volume ratio, the majority of Li ions are likely to diffuse on the surface of particles. After completion of the reaction, the powder is heat treated in a controlled atmosphere at a relatively low temperature to form the desired phase. In contrast to solid state synthesis techniques, our novel process leads to an ultrafine particle size with precise control of the composition. The schematic of the process to produce nanostructured $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is shown in Fig. 3. The diffusion of Li ions into particles depends upon the three factors:

- (1) The synthesis method utilizes an organic solvent, and thus prevents the formation of hydration layer around the dopant cation. A hydration layer increases the overall size of cations, and as a result, inhibits diffusion of cations in nanoparticles at low temperatures ($\leq 200^\circ\text{C}$) and at one atmospheric pressure. However, typically, in case of a hydrothermal process, inorganic salts of different constituents are dissolved in

water, and the solution is heated at high temperatures and pressures to promote precipitation of hydrated oxide particles.

(2) Precursor oxide nanoparticles have high surface to volume ratio and diffusion distances are an order of magnitude shorter than that of micron-sized particles; consequently, Li-ions can diffuse in nanoparticles at significantly lower temperatures than in micron-sized particles.

(3) The diffusion of dopants in host oxides is also dependent on the structure of the oxide. If the oxide has an open structure and unoccupied substitutional and interstitial sites and can easily accept or lose oxygen at low temperatures (e.g., TiO_2), it will be easier for dopant cations to diffuse in the host oxide without a destructive transformation. For example, we were able to diffuse Li^+ in nanoparticles of anatase TiO_{2-x} because anatase has unoccupied interstitial sites, and TiO_{2-x} can accept oxygen at low enough temperatures at high partial pressures of oxygen by the following reaction:



Therefore, the kinetics of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particle formation depends on the type of the solvent, solvent boiling point, which controls the refluxing temperature, and the primary particle size of TiO_2 powders. To investigate these factors, several experiments were performed.

Examples 1-3 Effect of the Solvent

In a first example attempts to synthesize $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders using water, $\text{LiOH}\cdot\text{H}_2\text{O}$ and *nano*- TiO_2 (average primary particle $\sim 20 - 25$ nm) were made. 0.425g of $\text{LiOH}\cdot\text{H}_2\text{O}$ was completely dissolved in 30 ml of water; subsequently, 1 g of *nano*- TiO_2 was added in the solution. After homogenously mixing nanopowder with the solution, it was refluxed for approximately 15 hrs. On completing the refluxing, water was evaporated. Dried powders were heat treated at 750°C for four hours in oxygen, but x-ray diffraction analysis revealed that the powders did not transform to the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ phase and contained a large proportion of unreacted TiO_2 material, along with other unidentified impurity peaks, suggesting that powders need to be heat-treated at much higher temperature. In a second example, similar results were also obtained for powders, which were synthesized using water, Li_2CO_3 and *nano*- TiO_2 . Li_2CO_3 and *nano*- TiO_2 were mixed in stoichiometric ratio.

On the other hand, in a third example, powders prepared by using methanol, LiNO_3 and *nano*- TiO_2 did not contain any unreacted TiO_2 powder, and the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was the predominant phase. In this example LiNO_3 (0.69 g) was dissolved in 20 ml of methanol. 1 g of *nano*- TiO_2 (average primary particle $\sim 20 - 25$ nm) was mixed with this solution, and the $\text{TiO}_2/\text{LiNO}_3/\text{methanol}$ mixture was refluxed for approximately 15 hrs. Excess amount of methanol was evaporated, and dried powder was heat-treated at 700°C for 4 hrs in O_2 .

Example 4- Effect of the Boiling Point of the Organic Solvent

The boiling point of organic solvents is observed to have a significant effect on the kinetics of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ phase formation. Nano- TiO_2 was reduced in a 95% Ar + 5% H_2 atmosphere at 300°C for 2 hrs to form TiO_{2-x} particles. $\text{Li}_y\text{TiO}_{(2+y/2-x)}/\text{LiNO}_3/\text{TiO}_{2-x}$ mixture, prepared in a hexanol solution (BP = 158°C), transforms to lithium titanate phases at a much lower temperature than that prepared in methanol (BP = 79°C). The $\text{Li}_y\text{TiO}_{(2+y/2-x)}/\text{LiNO}_3/\text{TiO}_{2-x}$ mixture prepared in a methanol solution and annealed at 650°C for 4 hrs in O_2 contains predominately rutile TiO_2 phase and a smaller amount of anatase and lithium titanate phases; on the other hand, on heating the $\text{Li}_y\text{TiO}_{(2+y/2-x)}/\text{LiNO}_3/\text{TiO}_{2-x}$ mixture, prepared in a hexanol solution, at the same temperature and time, a large proportion of lithium titanate phases – $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and LiTiO_2 – were formed. Furthermore, the mixture prepared in a hexanol solution on heating did not exhibit anatase peaks in the X-ray diffraction pattern.

Example 5- Effect of the TiO_2 Particle Size

On decreasing the particle size from micrometer to a nanometer scale, the diffusion distance of Li-ions reduces by an order of magnitude; consequently, Li-ions can diffuse into nanoparticles at much lower temperatures than those of coarse particles. To investigate the effect of the TiO_2 particle size on the reaction kinetics of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ phase formation, commercial coarse TiO_2 powders (particle size – 325 mesh size) were used to produce $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles by using the processing steps described in example 6

discussed below. Everything in the procedure was kept same except *nano*-TiO₂ powders were replaced with coarse TiO₂ powders. Powder X-ray diffraction reveals that a majority of TiO₂ has not been reacted, suggesting the importance of nanostructured TiO₂ in the synthesis of ultrafine Li₄Ti₅O₁₂ powders.

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Example 6- high boiling point organic solvent

This Example illustrates a preferred embodiment for the preparation of nanostructured (or ultrafine) Li₄Ti₅O₁₂ powders as follows:

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First, 2.14 g of LiNO₃ salt was added to 40 ml of hexanol, and the solution was stirred vigorously to dissolve the salt completely in hexanol in a single neck round-bottom flask. Next, 2.9 g of TiO₂ nanopowder with an average primary particle size in the range of 20 – 25 nm was added into the LiNO₃/hexanol solution. After homogenously mixing nanopowder with the solution, the mixed solution, while stirring, was refluxed at ~ 155 °C for 15 hrs. On completing the refluxing step, hexanol solvent was evaporated at an atmospheric pressure by heating the solution. The evaporated solvent was condensed in a flask. Powder in the flask was mixed with distilled water to completely remove any residual powder in the flask. Powder was dried on a hot plate to remove any residual water. Dried powder was heat-treated at 700 °C for 4 hrs in oxygen to produce the Li₄Ti₅O₁₂ phase. XRD pattern of the powder, Fig. 2, exhibits clearly that predominant phase is the cubic spinel Li₄Ti₅O₁₂. TEM micrographs of powders before the heat-treatment and after the heat-treatment are shown in Figs. 4 and 1, respectively.

As is well known the quantities set forth herein are for example only, such quantities can be scaled and adjusted in accordance with the teachings of this invention. The invention has been described with respect to preferred embodiments. However, as
5 those skilled in the art will recognize, modifications and variations in the specific details which have been described and illustrated may be resorted to without departing from the spirit and scope of the invention as defined in the appended claims

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